

## PATENT SPECIFICATION

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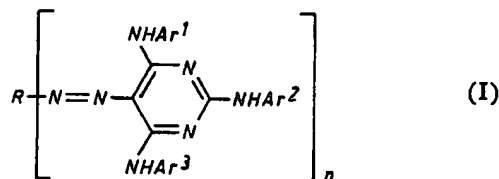
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2G2C7 2H5(72) Inventors IAN ALEXANDER MacPHERSON,  
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## (54) NEW AZO PIGMENTS

(71) We, CIBA-GEIGY AG, a Swiss Body Corporate, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to new azo pigments and their production.

According to the present invention there are provided valuable azo pigments of the general formula:

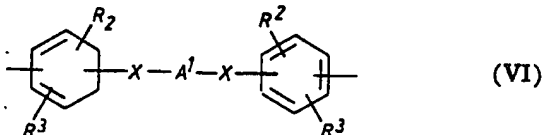


wherein R represents a carbocyclic or heterocyclic aromatic radical-containing group, which may be substituted by one or more non water-solubilising groups; Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup> are the same or different and represent a substituted or unsubstituted aryl group or a heterocyclic aromatic group; n is 1 or 2; and the indicated azo group is directly attached to an aromatic ring in R.

Since the colouring materials of the present invention are pigments, they are free of water-solubilising groups such as carboxyl and sulphonic acid groups.

When R represents an aryl group it may be, for example, a phenyl or phenylene group or a phenyl or phenylene group substituted by one or more halogen atoms, such as chlorine or bromine atoms, nitro groups, alkyl groups having 1 to 3 carbon atoms, or alkoxy groups having 1 to 3 carbon atoms. R may also represent a group comprising more than one aryl ring joined together by a direct bond or a linking group, or fused together, which rings may be unsubstituted or substituted by one or more halogen atoms, such as chlorine or bromine atoms, nitro groups, alkyl groups having 1 to 3 carbon atoms or alkoxy groups having 1 to 3 carbon atoms. Included in such groups comprising more than one aryl ring are groups of the formula —B—X—A—X—B in which A represents an alkylene group having 1 to 8 carbon atoms, which may be interrupted by a hetero atom, an arylene or aralkylene radical, B represents a carbocyclic or heterocyclic aromatic radical, especially a phenyl radical and X represents an oxygen or sulphur atom.

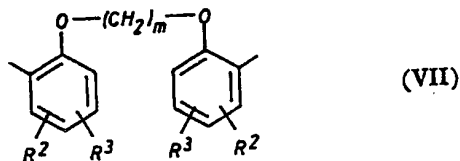
When R represents a group of the formula —B—X—A—X—B— it may be one of the formula:



in which X is oxygen or sulphur, A<sup>1</sup> is an alkylene group having 1 to 8 carbon atoms, a phenylene radical or a phenylene-bis-alkylene radical wherein the alkylene

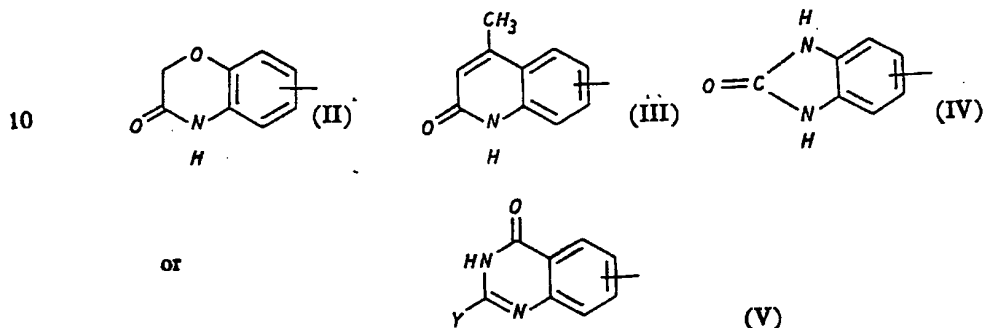
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groups have 1 to 4 carbon atoms,  $R^2$  and  $R^3$  represent hydrogen or halogen atoms, alkyl, alkoxy or alkylthio groups having 1 to 4 carbon atoms, alkoxy carbonyl or alkylcarbamoyl groups having 2 to 6 carbon atoms, carbamoyl or sulphonamoyl groups, alkylsulphonyl or alkylsulphonamoyl groups having 1 to 6 carbon atoms, phenyl-carbamoyl or phenylsulphonamoyl groups; and especially those of the formula:



wherein  $R^2$  and  $R^3$  are as defined above and  $m$  is a number from 1 to 4.

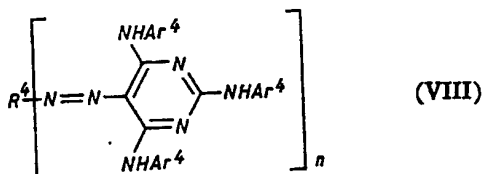
When  $R$  represents a heterocyclic radical it may be, for example, a group of the formulae:



which may be substituted with one or more halogen atoms or alkyl groups having 1 to 4 carbon atoms, wherein  $Y$  represents hydrogen or an alkyl or aryl group.

The groups  $Ar^1$ ,  $Ar^2$  and  $Ar^3$  are preferably phenyl groups or phenyl groups substituted with one or more halogen atoms, such as chlorine or bromine atoms, alkyl groups having 1 to 3 carbon atoms or alkoxy groups having 1 to 3 carbon atoms. Preferably  $Ar^1$ ,  $Ar^2$  and  $Ar^3$  are the same.

Pigments of particular interest are those of the formula:

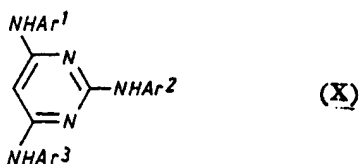


wherein when  $n$  is 1  $R^4$  represents a substituted phenyl group or a heterocyclic group of the formulae II, III, IV or V above, which may be substituted by one or more chlorine atoms and/or methyl groups, or when  $n$  is 2,  $R^4$  represents a group of the formula VII above and  $Ar^4$  represents a phenyl group or a phenyl group substituted with one or more chlorine or methoxy groups.

The pigments of the invention may be prepared by coupling 1 mole of a diazo or tetrazo derivative of a base of the formula:



where  $n$  is 1 or 2 with  $n$  moles of a coupling component of the formula:



Examples of bases, which may be used in the present invention, are 2-chloro-aniline, 2,4-dichloroaniline, 2,5-dichloroaniline, 2,4,5-trichloroaniline, 2,4,6-trichloro-aniline, 2-chloro-4-nitroaniline, 2-nitro-4-methylaniline, 2-methoxyaniline, 4-methoxy-aniline, 4-nitroaniline, 6-amino-quinazalone-4, 7-amino-6-methyl phenmorpholone-3, 5-amino-benzimidazalone, 6-amino-quinolone-2, 7-amino-6-methyl-phenmorpholone-2, 5-amino-6-methylbenzimidazolone, 6-chloro-7-amino-4-methyl-quinolone-2 and 4,6-dimethyl-7-amino-quinolone-2. 4,4'-Diaminodiphenyl, 3,3'-Dichloro-4,4'-diaminodi-phenyl, 3,3'-Dimethyl-4,4'-diaminodiphenyl, 3,3'-Dimethoxy-4,4'-diaminodiphenyl, 3,3'-Diethoxy-4,4'-diaminodiphenyl, 3,5,3',5'-Tetrachloro-4,4'-diaminodiphenyl, 3,3'-Diamino-diphenylketone, 3,3'-Diamino-4,4'-dichloro-diphenylketone, 3,3'-Diamino-4,4'-dimethoxydiphenylketone, 4,4'-Diamino-diphenylsulphone, 3,3'-Diamino-4,4'-dichloro-diphenylsulphone, 3,3'-Diamino-4,4'-dimethoxy-diphenylsulphone, 3,3'-Diamino-di-phenylmethane, 4,4'-Diamino-diphenylmethane, 4,4'-Diamino-3,3'-dichloro-diphenyl-methane, 3,3'-Diamino-4,4'-dichloro-diphenylmethane, 4,4'-Diamino-diphenylsulfide, 4,4'-Diamino-diphenylether, 4,4'-Diamino-benzoylaniline, 4,4'-Diamino-2-ethoxy-benzoylaniline, 3,3'-Diamino-2,2'-dimethoxy-benzoylaniline, 4,4'-Diamino-diphenylurea, 4,4'-Diamino-3,3'-dimethoxy-diphenylurea, 4,4'-Diaminostilbene, 4,4'-Diamino-azo-benzene, 2-methyl-4,4'-diaminoazobenzene, 2-Methoxy-4,4'-diaminoazobenzene, 2,5-Dimethyl-4,4'-diaminoazobenzene, 2,5,2'-Trimethyl-4,4'-diaminoazobenzene, 3-Methyl-2'-methoxy-4,4'-diaminoazobenzene, 3-Chloro-2'-methyl-4,4'-diaminoazo-benzene, 4 - Chloro - 3,4' - diaminoazobenzene, 2 - Chloro - 4,3' - diaminoazo-benzene, 2 - Methyl - 4,3' - diaminoazobenzene, 2 - Methoxy- 4,4' - diaminoazo-benzene, 4,4' - Diamino - phenyl - 1 - azo - naphthalene - 1, 2,2' - Diaminodi-benzyl, 1,4 - Diaminonaphthalene, 1,5 - Diaminonaphthalene, 2,7 - Diamino-fluorene, 4,11 - Diaminofluoranthene, 3,8 - Diaminopyrene, 2,8 - Diamino-chrysene, 2,6 - Diaminocarbazole, 2,7 - Diaminodiphenyleneoxide, 2,6 - Diamino-diphenyleneoxide, 2,7 - Diaminodiphenylenesulphone, 2 - (4' - Aminophenyl) - 6-aminobenzthiazole, 1,4 - Phenylenediamine, 2 - Chloro - 1,4 - phenylenediamine, 2,5 - Dichloro - 1,4 - phenylene - diamine, 2 - Methyl - 1,4 - phenylene - diamine, 2,5 - Dimethyl - 1,4 - phenylene - diamine, 2 - Methoxy - 1,4 - phenylene - diamine, 2,5 - Dimethoxy - 1,4 - phenylene - diamine, 2 - Chloro - 5 - methyl - 1,4 - phenyl-ene - diamine, 2 - Chloro - 5 - methoxy - 1,4 - phenylene - diamine. These bases are known compounds.

The coupling is suitably carried out by gradual addition of the aqueous diazonium salt solution to the solution of the coupling component in a water-miscible organic solvent such as, for example, dimethylformamide, or by gradual addition of the aqueous acid solution of the coupling component to the acid solution of the diazonium salt. The coupling is suitably carried out at a pH value of 4 to 6, although coupling can be effected outside this pH range.

The pH value is advantageously adjusted by addition of a buffer. Buffers which can be used are, for example, the salts, especially the alkali metal salts, of formic acid, phosphoric acid or, especially, acetic acid. The acid solution of the coupling component suitably contains a wetting agent, dispersing agent or emulsifier, for example an alkylsulphonate, such as dodecylbenzenesulphonate or the sodium salt of 1,1'-naphthylmethanesulphonic acid, polycondensation products of alkylene oxides, such as the reaction product of ethylene oxide with p-tert-octylphenol and also alkyl esters of sulphoricinoleates, for example n-butyl sulphoricinoleate. The dispersion of the coupling component can also advantageously contain protective colloids, for example methylcellulose or minor amounts of inert sparingly water-soluble or water-insoluble organic solvents, for example optionally halogenated or nitrated aromatic hydrocarbons, such as benzene, toluene, xylene, chlorobenzene, dichlorobenzene or nitrobenzene, as well as aliphatic halogenated hydrocarbons such as, for example, carbon tetrachloride or trichloroethylene, and also water-miscible organic solvents, such as acetone, methyl ethyl ketone, methanol, ethanol or isopropanol, especially dimethyl-formamide.

By virtue of their insolubility, the pigments obtained can be isolated from the

reaction mixtures by filtration. It may prove to be advantageous to after treat the resulting pigments with an organic solvent which preferably boils above 100° C. Benzenes substituted by halogen atoms, alkyl groups or nitro groups, such as xylenes, chlorobenzene, o-dichlorobenzene or nitrobenzene, and also pyridine bases, such as pyridine, picoline or quinoline, as well as ketones, such as cyclohexanone, ethers, such as ethylene glycol monomethyl ether or monoethyl ether, amides, such as dimethylformamide or N-methyl-pyrrolidone, and also dimethylsulphoxide, prove to be particularly suitable.

The after-treatment is preferably carried out by heating the pigment, in the solvent, to 100—250° C., whereupon a coarsening of the particle size occurs in many cases, this having a favourable effect on the fastness to light and to migration of the pigments obtained.

Alternatively, it may be desirable that the pigments be obtained in a very finely divided form. In this case, after-treatments with high-boiling solvents would be avoided and wood rosin derivatives such as abietic acid and hydrogenated abietic acids could be incorporated before, during or after the formation of the pigment. Similar treatments with long chain aliphatic amines such as stearylamine may be used either alone or in conjunction with wood rosin derivatives and surface active agents.

The coupling can also be carried out by continuously combining an acid solution of the diazonium salt with an acid solution of the coupling component in a mixing nozzle, whereupon immediate coupling of the components takes place. The resulting dyestuff dispersion is continuously withdrawn from the mixing nozzle and the dyestuff is separated off by filtration.

Instead of the diazonium salts, the corresponding diazoamino compounds can also be used. These are obtained according to a known process by coupling an aryldiazonium salt with a primary amine or preferably with a secondary amine. The most diverse amines are suitable for this purpose, for example aliphatic amines such as methylamine, ethylamine, ethanolamine, propylamine, butylamine, hexylamine and especially dimethylamine, diethylamine, diethanolamine, methylethanolamine, dipropylamine or dibutylamine, aminoacetic acid, methylaminoacetic acid, butylaminoacetic acid, aminoethanesulphonic acid, methylaminoethanesulphonic acid, guanylethanesulphonic acid,  $\beta$ -aminoethylsulphuric acid, alicyclic amines, such as cyclohexylamine, N-methylcyclohexylamine and dicyclohexylamine, aromatic amines, such as 4-aminobenzoic acid, sulphaniilic acid, 4-sulpho-2-aminobenzoic acid, (4-sulphophenyl)-guanidine, 4-N-methylaminobenzoic acid, 4-ethylaminobenzoic acid, 1-aminonaphthalene-4-sulphonic acid, 1-aminonaphthalene-2,4-disulphonic acid, heterocyclic amines, such as piperidine, morpholine, pyrrolidine and dihydroindole, and finally also sodium cyanamide or dicyandiamide.

As a rule, the diazoamino compounds obtained are sparingly soluble in cold water and can, if necessary after salting out, be separated in a crystalline form from the reaction medium. In many cases, the moist press cakes can be used for the further reaction. In some cases, it can prove desirable to dehydrate the diazoamines by vacuum drying prior to the reaction.

The coupling of the diazoamino compounds with the coupling component is carried out in an organic solvent, for example chlorobenzene, o-dichlorobenzene, nitrobenzene, pyridine, ethylene glycol, ethylene glycol monoethyl ether or monomethyl ether, dimethylformamide, formic acid or acetic acid.

If water-miscible solvents are used it is not necessary to use the diazoamino compounds in an anhydrous form. For example, the water-moist filter cakes can be used.

The coupling is suitably carried out under warm conditions, preferably at temperatures between 80 and 180° C., in an acid medium, and in general takes place very rapidly and completely. If neutral solvents are used, the addition of an acid, for example hydrogen chloride, sulphuric acid, formic acid or acetic acid, is of advantage. Because of their insolubility, the pigments obtained can be isolated from the reaction mixture by filtration. An after-treatment with organic solvents, such as is sometimes necessary in the case of pigments which are obtained by the aqueous coupling method, is therefore unnecessary in most cases.

Finally, the coupling can also be completed by suspending the amine to be diazotised, together with the coupling component, in the molar ratio of 1:1, in an organic solvent and treating the mixture with a diazotising agent, especially an ester of nitrous acid, such as methyl nitrite, ethyl nitrite, butyl nitrite, amyl nitrite or octyl nitrite.

The new colourants are valuable pigments which can be used in a finely divided form, for pigmenting high molecular weight organic material, for example cellulose

ethers and cellulose esters, such as ethylcellulose, nitrocellulose, cellulose acetate, cellulose butyrate, natural resins or synthetic resins, such as polymerisation resins or condensation resins, for example aminoplasts, especially urea-formaldehyde and melamineformaldehyde resins, alkyd resins, phenoplasts, polycarbonates, polyolefines, such as polystyrene, polyvinyl chloride, polyethylene, polypropylene, polyacrylonitrile, polyacrylic acid esters, polyamides, polyurethanes or polyesters, rubber, casein, silicone and silicone resins, individually or as mixtures.

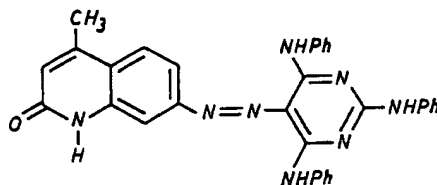
It is immaterial whether the high molecular weight compounds mentioned are in the form of plastic masses or melts or in the form of spinning solutions, lacquers, paints or printing inks. Depending on the end use, it proves to be advantageous to use the new pigments as pigment powders or in the form of preparations in combination with quantities of a carrier compatible with the medium to be pigmented. The pigments of the invention are particularly suitable for use in the production of printing inks.

The pigments of the present invention are high strength bright yellow to red pigments which are simple to prepare and have a remarkably low solubility in water.

The invention is illustrated by the following Examples, in which parts are parts by weight (unless otherwise stated). Parts by weight bear the same relationship to parts by volume as do kilograms to litres.

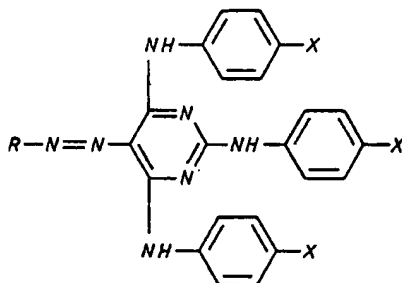
#### EXAMPLE 1.

17.4 Parts of 4-methyl-7-amino-quinolone-(2) were diazotised in 25 parts by volume hydrochloric acid using 6.9 parts of anhydrous sodium nitrite at 0° C. 30 Parts of hydrated sodium acetate were added to buffer the solution at pH 4—5. 36 Parts of 2,4,6-tris (anilino) pyrimidine were dissolved in dilute acetic acid plus a small quantity of a surfactant. This solution was slowly run into the buffered diazo solution. The resulting pigment suspension was filtered off and dried at 50° C. for 16 hours, to yield 53.5 parts of a bright orange pigment of the formula:



#### EXAMPLES 2—37.

Following the procedure of Example 1, but using the appropriate bases and coupling components indicated in the following Table, pigments were obtained having the colour given. The pigments produced had the formula:



TABLE

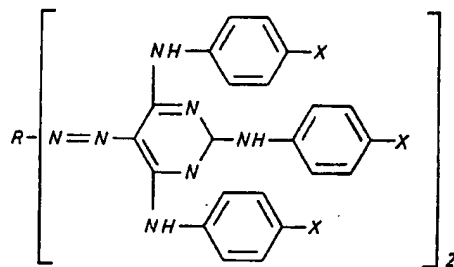
Example	Base	X	Shade
2	6-amino-7-methyl-phenmorpholone-3	H	orange
3	6-methyl-7-amino-phenmorpholone-3	H	red
4	4-methyl-7-amino-quinolone-2	H	orange
5	5-amino-benzimidazolone	H	yellow
6	5-amino-6-methyl-benzimidazolone	H	yellow
7	4-methyl-6-chloro-7-amino-quinolone-2	H	orange-red
8	4,6-dimethyl-7-amino-quinolone-2	H	orange
9	2-chloroaniline	H	red
10	2,4-dichloroaniline	H	orange
11	2,5-dichloroaniline	H	orange-red
12	2,4,5-trichloroaniline	H	orange
13	2-chloro-4-nitroaniline	H	red-violet
14	2-nitro-4-methylaniline	H	red-orange
15	2-methoxyaniline	H	red
16	4-methoxyaniline	H	red-orange
17	4-nitroaniline	H	red
18	2,4,6-trichloroaniline	H	red
19	5-amino-benzimidazolone	Cl	yellow-orange
20	6-amino-quinazolone-4	Cl	yellow-orange
21	4-methyl-7-amino-quinolone-2	Cl	orange
22	6-methyl-7-amino-phenmorpholone-3	Cl	orange
23	5-methyl-6-amino-benzimidazolone	Cl	yellow-orange
24	4-methyl-5-chloro-7-amino-quinolone-2	Cl	orange
25	4,6-dimethyl-7-amino-quinolone-2	Cl	orange
26	4-methyl-7-amino-quinolone-2	OCH <sub>3</sub>	orange-red
27	6-amino-quinazolone-4	OCH <sub>3</sub>	red-orange
28	5-amino-benzimidazolone	OCH <sub>3</sub>	yellow
29	6-methyl-7-amino-phenmorpholone-2	OCH <sub>3</sub>	orange

TABLE (Continued)

Example	Base	X	Shade
30	5-methyl-6-amino-benzimidazolone	OCH <sub>3</sub>	orange
31	4-methyl-6-chloro-7-amino-quinolone-2	OCH <sub>3</sub>	orange-red
32	4,6-dimethyl-7-amino-quinolone-2	OCH <sub>3</sub>	red
33	6-amino-7-chlor-4-methyl-quinolone-2	H	orange
34	7-amino-4,8-dimethyl-quinolone-2	H	yellow-orange
35	7-amino-4,8-dimethyl-quinolone-2	Cl	yellow
36	7-amino-4,8-dimethyl-quinolone-2	OCH <sub>3</sub>	orange-red
37	2-methyl-3-(4'-aminophenyl)-4(3H)-quinazolone	H	yellow

## EXAMPLES 38—42.

Following the procedure of Example 1, but using the appropriate bases and coupling components indicated in the following Table, pigments were obtained having the colour given. The pigments produced had the formula:



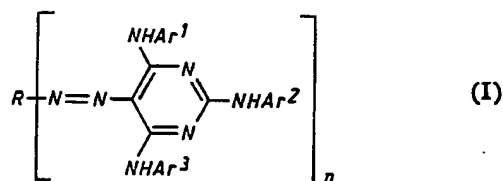
Example	Base	X	Shade
38		H	yellow
39		H	yellow
40		H	yellow
41		H	yellow
42		H	yellow

## EXAMPLE 43.

150 Parts of the product from Example 1 was mixed with 175 parts of a long oil terephthalic alkyd with viscosity of about 20 to 30 poise and 175 parts of a modified phenolic resin with a viscosity of about 3000 poise. The paste was then ground on a Cox Pilot 3 Roll Mill giving first a low pressure wetting pass and subsequently several high pressure passes. The resulting ink was free from undispersed particles as shown on a Hegman Gauge and had good flow. When printed on a typical lithographic press it gave a bright, strong, orange print.

## WHAT WE CLAIM IS:—

1. An azo pigment of the general formula (I)



wherein R represents a carbocyclic or heterocyclic aromatic radical-containing group, which may be substituted by one or more non water-solubilising groups; Ar<sup>1</sup>, Ar<sup>2</sup>, Ar<sup>3</sup> are the same or different and represent a substituted or unsubstituted aryl group or a heterocyclic aromatic group; n is 1 or 2; and the indicated azo group is directly attached to an aromatic ring in R.

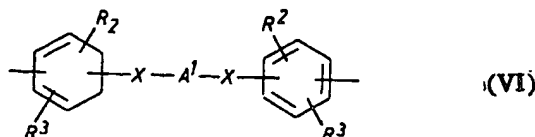
2. An azo pigment as claimed in Claim 1, in which R represents a phenyl or



phenylene group, or a phenyl or phenylene group substituted by one or more halogen atoms, nitro groups, or alkyl or alkoxy groups having 1 to 3 carbon atoms.

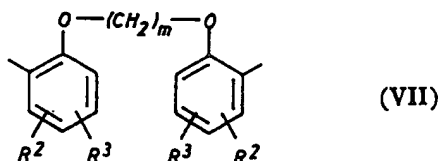
3. An azo pigment as claimed in Claim 1, in which R represents a radical of the formula  $\text{—B—X—A—X—B—}$  in which A represents an alkylene group having 1 to 8 carbon atoms, which may be interrupted by a hetero atom, an arylene or aralkylene radical, B represents a carbocyclic or heterocyclic aromatic radical and X represents an oxygen or sulphur atom.

4. An azo pigment as claimed in Claim 3, in which R represents a group of the formula VI



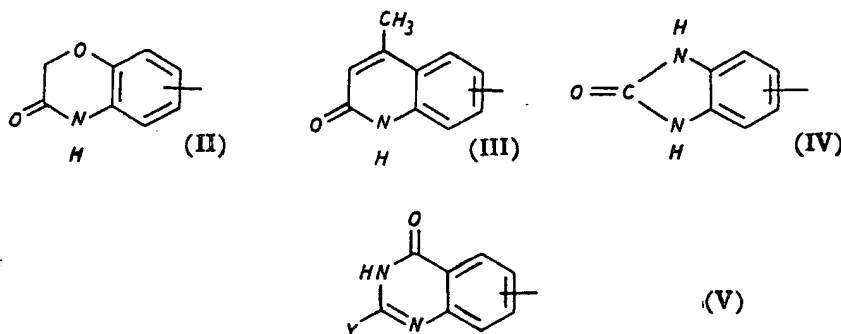
in which X is oxygen or sulphur, A' is an alkylene group having 1 to 8 carbon atoms, a phenylene radical or a phenylene-bis-alkylene radical wherein the alkylene groups have 1 to 4 carbon atoms, R<sup>2</sup> and R<sup>3</sup> represent hydrogen or halogen atoms, alkyl, alkoxy or alkylthio groups having 1 to 4 carbon atoms, alkoxycarbonyl or alkylcarbamoyl groups having 2 to 6 carbon atoms, carbamoyl or sulphamoyl groups, alkylsulphonyl or alkylsulphamoyl groups having 1 to 6 carbon atoms, phenylcarbamoyl or phenylsulphamoyl groups.

5. An azo pigment as claimed in Claim 3 or 4 in which R represents a group of the formula VII



wherein R<sup>2</sup> and R<sup>3</sup> are as defined above and m is a number from 1 to 4.

6. An azo pigment as claimed in Claim 1, in which R represents a group of the formula

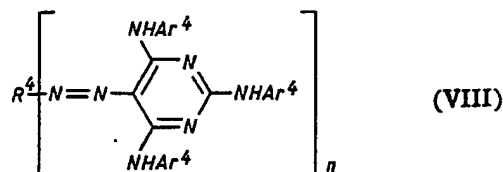


which may be substituted with one or more halogen atoms or alkyl groups having 1 to 4 carbon atoms, wherein Y represents a hydrogen or an alkyl or aryl group.

7. An azo pigment as claimed in any preceding claim in which the groups Ar<sup>1</sup>, Ar<sup>2</sup>, and Ar<sup>3</sup> are phenyl groups or phenyl groups substituted with one or more halogen atoms or alkyl or alkoxy groups having 1 to 3 carbon atoms.

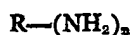
8. An azo pigment as claimed in any preceding claim in which Ar<sup>1</sup>, Ar<sup>2</sup> and Ar<sup>3</sup> are the same.

9. An azo pigment as claimed in Claim 1 which has the formula VIII



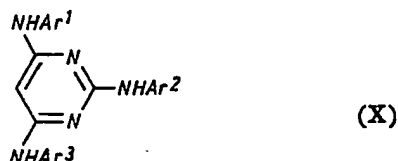
wherein when  $n$  is 1  $\text{R}^4$  represents a substituted phenyl group or a heterocyclic group of the formulae II, III, IV or V above, which may be substituted by one or more chlorine atoms and/or methyl groups, or when  $n$  is 2,  $\text{R}^4$  represents a group of the formula VII above and  $\text{Ar}^4$  represents a phenyl group or a phenyl group substituted with one or more chlorine or methoxy groups.

10. A process for preparing a pigment of the general formula I, defined in Claim 1 which comprises coupling 1 mole of a diazo or tetrazo derivative of a base of the formula IX



IX

where  $n$  is 1 or 2, with  $n$  moles of a coupling component of the formula X



wherein  $\text{R}$ ,  $\text{Ar}^1$ ,  $\text{Ar}^2$  and  $\text{Ar}^3$  are as defined in Claim 1.

11. A modification of the process as claimed in Claim 10, in which a diazoamino or tetrazoamino derivative of the base is used, and the coupling is carried out in an organic solvent.

12. A process as claimed in Claim 10 or 11, in which the coupling component is 2,4,6-tris (anilino) pyrimidine, 2,4,6-tris (4-chloroanilino) pyrimidine or 2,4,6-tris (4-methoxyanilino) pyrimidine.

13. An azo pigment as claimed in Claim 1, substantially as hereinbefore described with reference to any one of Examples 1 to 42.

14. A process for preparing an azo pigment as defined in Claim 1, substantially as hereinbefore described with reference to any one of Examples 1 to 42.

15. A composition comprising a high molecular weight organic material and a pigment as claimed in any one of Claims 1 to 9 or 13.

16. A process for colouring a high molecular weight organic material which comprises incorporating therein a pigment as claimed in any one of Claims 1 to 9 or 13.

17. A composition as claimed in Claim 15, substantially as hereinbefore described with reference to Example 43.

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- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☒ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

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